The symmetry of the superconducting order parameter in $PuCoGa_5$

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The symmetry of the superconducting order parameter in single-crystalline $PuCoGa_5$ (T_c = 18.5 K) is investigated via zero- and transverse- field muon spin relaxation (μSR) measurements, probing the possible existence of orbital and/or spin moments (time reversal-symmetry violation TRV) associated with the superconducting phase and the in-plane magnetic-field penetration depth $\lambda(T)$ in the mixed state, respectively. We find no evidence for TRV, and show that the superfluid density, or alternatively, $\Delta\lambda(T) = \lambda(T) - \lambda(0)$, are $\propto T$ for $T/T_c \leq 0.5$. Taken together these measurements are consistent with an even-parity (pseudo-spin singlet), d-wave pairing state.

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Because f-electrons may exist at the boundary between localization and itinerancy, f-electron compounds present an extreme challenge for many-body physics. For example, Pu metal sits midway between 'itinerant' Np and 'localized' Am [1], while some theories for the δ-phase of Pu postulate that only one out of five of its 5-f electrons are delocalized [2]. Delocalization is a key ingredient for heavy fermion behavior, which arises from strong f-electron conduction-electron hybridization. A new class of tetragonal heavy-fermion compounds Ce_nMIn_{3n+2}, with $n = 1, 2$, has been under considerable investigation for the wide variety of magnetic and unconventional superconducting behaviors which it exhibits [3]. The superconductivity in these compounds occurs below $\sim$ 2 K, arising out of a normal state in close proximity to an antiferromagnetic quantum critical point and possessing a large Sommerfeld constant (γ = 0.7 J/mol-K^2 in $CeIrIn_5$). The recent discovery [4] of superconductivity with an order-of-magnitude higher critical temperature in the same structural class of materials, but possessing Pu instead of Ce, is consequently both exciting and significant. $PuCoGa_5$ becomes superconducting below $T_c = 18.5$ K from a normal state with a relatively modest $\gamma = 77$ mJ/mol-K^2 [4]. Photoemission suggests the f-electrons in $PuCoGa_5$ are between localized and itinerant [5].

The superconducting pairing interaction in heavy fermion materials is believed to arise from antiferromagnetic spin fluctuations, and a similar pairing mechanism has been postulated for the light-mass cuprate superconductors [6]. This led to the speculation that $PuCoGa_5$ might be a bridging material between heavy fermions and the cuprates [4]. Recent electronic structure calculations [7] for $PuCoGa_5$ show 2-dimensional Fermi surfaces which could support spin-fluctuation-mediated superconductivity and, hence, d-wave pairing [6]. However, key measurements to confront these ideas are lacking; hence, tests of the symmetry of the superconducting order parameter in $PuCoGa_5$ are of supreme importance.

This Letter reports muon spin relaxation experiments (μSR) in single-crystal $PuCoGa_5$ designed to explore two aspects of its superconductivity: (1) a possible violation of time-reversal symmetry (TRV), indicated by small, spontaneous magnetic fields below T_c, and (2) the temperature dependence and magnitude of its superconducting penetration depth λ. To date no direct spectroscopic probes of these quantities have been reported. In these experiments spin-polarized positive muons ($\mu^+, S = 1/2$) are stopped in the sample and precess in the local magnetic field **B** until they undergo a parity-violating weak decay $\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu_\mu}$ (lifetime τ_μ=2.2μs). The time-dependence of the polarization, monitored via the positron decay anisotropy, yields information about the local field inhomogeneity and fluctuation spectrum [8].

Samples were grown from excess Ga flux [4], forming flat plates with the c-axis normal to the crystal face. Two crystals measuring $\sim 5{\times}6$mm^2 in total area and $\sim$1/2mm thick were encapsulated in a 70μm thick Kapton coating, and then attached and sealed under He atmosphere inside a titanium cell having a 50μm Ti-foil beam window and attached to a continuous-flow He cold-finger cryostat. The dual encapsulation was undertaken to prevent possible radioactive contamination.

Conventional time-differential μSR experiments were performed at the M20 channel at TRIUMF, Vancouver, Canada, only 3 weeks after the crystals were prepared. Thus, there was no measurable degradation of T_c due to radiation damage from Pu decay (half-life $\sim 2.4 \times 10^4$ y). Surface muons (momenta $\sim$ 29 MeV/c) were implanted into the sample with their spins perpendicular to their momenta, in the plane of the sample face. Approximately 1/3 of the muons stopped in the sample, the remaining fraction in the Ti sample holder. A negligible fraction stopped in the Ti window or the Kapton coating. The background signal obtained from an empty Ti holder in either zero applied field (ZF) or 600 Oe applied trans-

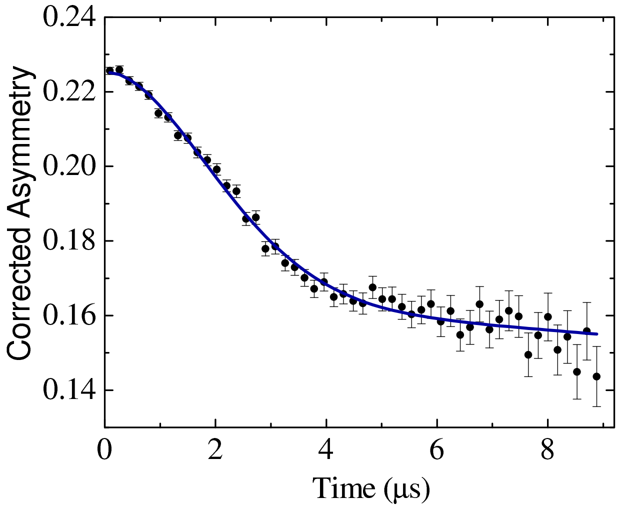

FIG. 1: A representative zero field spin relaxation spectrum at T=4 K. The solid line is a fit to a dynamic Gaussian Kubo-Toyabe relaxation function and a background from muons stopped in the Ti cell.

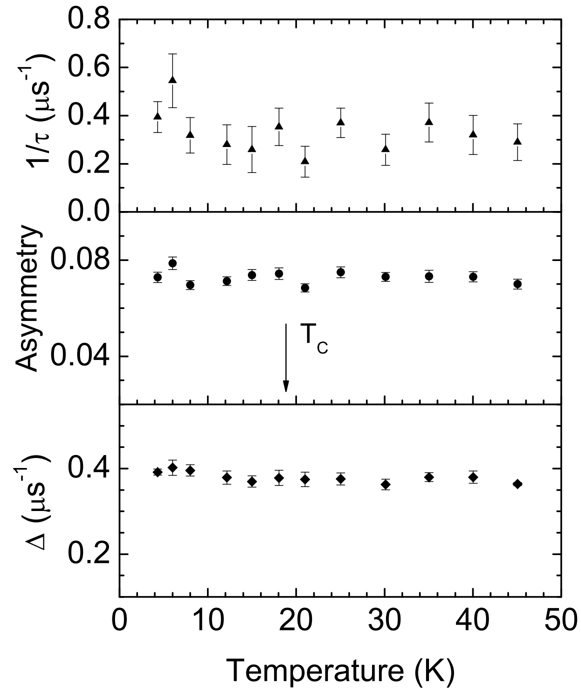

FIG. 2: Temperature dependencies of inverse correlation time $1/\tau$, amplitude and field width Δ obtained from fitting the ZF spectra to a dynamic Gaussian Kubo-Toyabe relaxation function.

verse to the muon spin (TF) was well characterized by a Gaussian relaxation function $G_{\mathrm{Ti}}(t) = \exp(-1/2\sigma_{\mathrm{Ti}}^2 t^2)$ with $\sigma_{\mathrm{Ti}} \approx 0.03\mu\mathrm{s}^{-1}$. For ZF experiments the residual field was reduced to ≤ 10 mOe using trim coils.

Figure (1) shows a representative ZF spin relaxation spectrum at T=4K, corrected for differences in the positron counters' efficiencies and solid angles. All of the ZF spectra – above and below T_{c} – were very similar. Between $T = 3 - 45$ K the overall relaxation is well described by the sum of $G_{\mathrm{Ti}}(t)$ and a *dynamic* Gaussian Kubo-Toyabe spin relaxation function [8] $G_{KT}(t, \Delta, \tau)$, with static rate Δ due to a distribution of Co and Ga nuclear dipolar fields and dynamic rate τ. The latter is produced by slow field dynamics and/or muon motion, as also seen in $\mathrm{CeCoIn_5}$ and $\mathrm{CeIrIn_5}$ [9]. In $\mathrm{PuCoGa_5}$ these fluctuations are sufficient to suppress the long-time tail of G_{KT} (which approaches $1/3A_0G_{KT}(t=0)$ when $\tau = \infty$), but only slightly affect the initial Gaussian relaxation. The temperature dependencies of τ^{-1}, relaxing amplitude and rate Δ are shown in Fig. 2. No temperature dependence is seen between $T = 3 - 45$ K.

Transverse field μSR locally probes the magnetic field distribution in the vortex state of superconductors [10], which is characterized by λ and the coherence length ξ_0, estimated to be $\xi_0 \sim 2.1$ nm from the temperature dependence of the upper critical field H_{c2} near T_{c} [4]. Field-cooled TF measurements were carried out in $H_0 = 600$ Oe field applied parallel to the c-axis. This field is at least twice the lower critical field $H_{\mathrm{c1}} \approx 300$ Oe reported previously [4] and $4 - 5\times$ that implied by our measurements of $\lambda(0)$ ($H_{\mathrm{c1}} \propto \ln(\lambda/\xi_0)/\lambda^2$), as discussed below. Precession spectra were fit to the sum of two terms, corresponding to muons stopping in the sample and Ti cell, respectively:

$$A_0 G_{\mathrm{z}}(t) = A\cos(\omega t + \phi)P(t) + A_{\mathrm{Ti}}\cos(\omega_{\mathrm{Ti}} t + \phi)\exp(-\sigma_{\mathrm{Ti}}^2 t^2/2). \quad (1)$$

The temperature dependence of σ for a Gaussian $P(t) = \exp(-\sigma^2 t^2/2)$ is shown in Fig. 3a. One sees that σ is much larger than $\sigma_{\mathrm{Ti}} \approx 0.03\mu\mathrm{s}^{-1}$ at all measured temperatures; thus, the two precession signals in Eq. (1) were easily separated. Fig. 3a also shows that σ increases sharply below $T_{\mathrm{c}} = 18.5$ K due to the increasing field inhomogeneity caused by the superconducting flux lattice, and increases linearly within the statistical errors below about 12 K.

A Gaussian time distribution implies a Gaussian field distribution, whereas in a single crystal the field distribution is expected to be asymmetric [11]. The quality of the Gaussian fits is illustrated in Fig. 4 for data taken at T = 4K. Here the $G_{\mathrm{z}}(t)$ data (Eq. 1) from $t = 3-10\mu$s were fit separately, and this long-time Ti signal was then subtracted from the total spectrum, leaving only the signal from the sample in the superconducting state. One sees that the Gaussian form for $P(t)$ gives a satisfactory fit. Thus, the absence of the expected asymmetric field distribution is probably due to the large

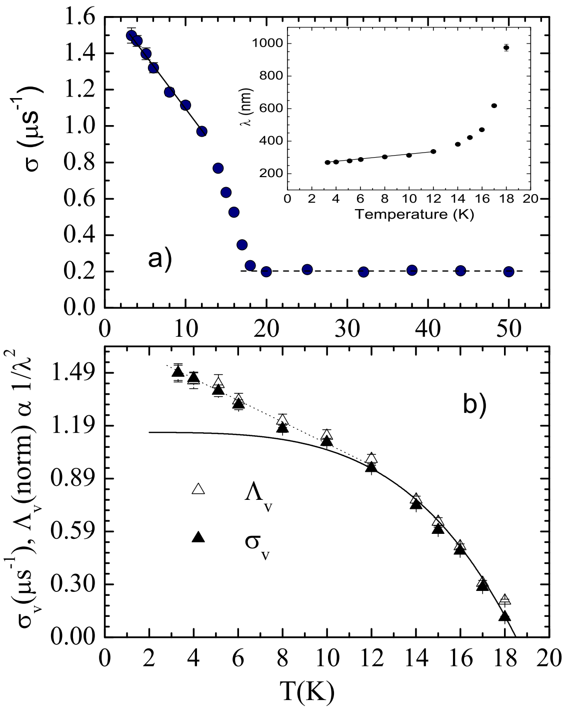

FIG. 3: a) Temperature dependence of μSR Gaussian TF rate $\sigma(T)$. (See Eq. (1) and discussion in text.) The average baseline σ_n above T_c is indicated by the dashed line; the solid straight line shows $\sigma \sim T$ below 12 K. The inset shows $\lambda(T)$ obtained from the linewidth $\sigma_v(T)$ and Eq. (2). The solid line is a linear fit between $3-12$ K. b) Rates from Gaussian (σ_v) and exponential (Λ_v - normalized to σ_v at 3.3 K) forms for $P(t)$ in Eq. (1) have the same temperature dependence below T_c. The curve is the result for the two-fluid model (s-wave), with $T_c = 18.5$ K and $\sigma_v = 1.15\mu s^{-1}$, determined to fit the data for $T \geq 12$ K. The straight dotted line illustrates $\sigma_v(T), \Lambda_v(T) \propto T$ for $T \leq 12$ K.

$\kappa = \lambda(0)/\xi_0 \approx 100$ value, together with the possibility that the flux lattice is distorted somewhat by radiation-induced pinning centers [11].

We now discuss the data with regard to the superconducting and magnetic properties of $PuCoGa_5$, beginning with the ZF results. First, the absence of any temperature dependence below 45 K in the parameters shown in Fig. 2 is strong evidence that there is no static electronic magnetism. The shape of the observed short-time Gaussian relaxation shown in Fig. 1 is consistent with static nuclear-dipolar broadening. (If this relaxation were instead due to damped, coherent precession from magnetic order, we estimate an ordered moment $< 5\times10^{-3}\mu_B$, which is $\ll 0.68\mu_B$ obtained from the susceptibility [4].) Assuming that muons occupy the same sites as in $CeRhIn_5$ [12], we estimate a ZF nuclear-dipolar linewidth of about 0.29 μs^{-1} for both of the hypothetical

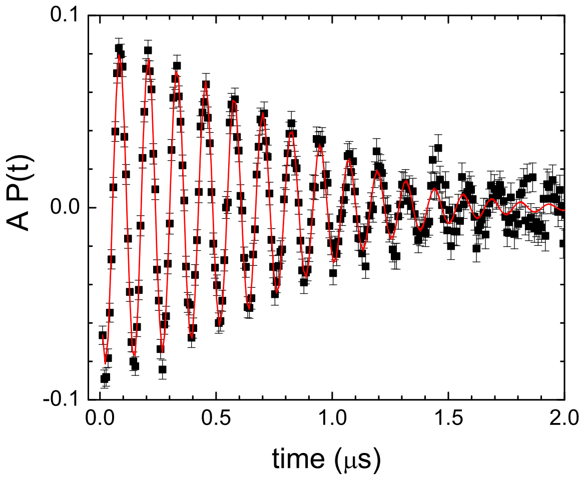

FIG. 4: Muon TF precession signal at $T = 4$ K. The data from $t = 3 - 10\mu s$ has been subtracted to show the inhomogeneous relaxation produced by the flux lattice in the superconducting state. The solid line is a fit for a Gaussian $P(t)$ in Eq. (1).

$(1/2, 1/2, 1/2)$ and $(0, 1/2, 0)$ sites . This is about 25% smaller than observed, indicating a different site occupancy from $CeRhIn_5$. Note, however, that none of our conclusions concerning the superconducting state depend at all on knowing the muon site(s).

In TF measurements the μSR rate from the vortex lattice σ_v measures the width of the rms field distribution $\langle\Delta B^2\rangle$: $\sigma_v = \gamma_\mu\langle\Delta B^2\rangle^{1/2}$, where $\gamma_\mu = 8.516\times10^8$ s^{-1} T^{-1} is the muon gyromagnetic ratio. The $\langle\Delta B^2\rangle$ is related to λ through the expression (assuming a hexagonal vortex lattice and $H_0 \ll H_{c2}$) [11]:

$$\sigma_v \propto \langle\Delta B^2\rangle^{1/2} = (0.00371)^{1/2}\Phi_0/\lambda^2 \propto \eta_s/m^* \qquad (2)$$

where $\Phi_0 = hc/2e = 2.07\cdot10^{-7}$ G·cm^2 is the magnetic flux quantum, η_s the superfluid density and m^* the in-plane effective mass [13].

The temperature dependence of σ_v is obtained by subtracting the temperature-averaged normal-state linewidth σ_n from the σ shown in Fig. 3a: $\sigma_v^2 = \sigma^2 - \sigma_n^2$, where $\sigma_n = 0.20$ μs^{-1}. This assumes that the linewidths σ_v and σ_n arise from independent sources, which they do. To check the effect of the form of $P(t)$ in Eq. (1) on the temperature dependence of the penetration depth, the time spectra were also fit using $P(t) = \exp(-\Lambda t)$, and an analogous subtraction procedure was used (suitable for exponentials), namely $\Lambda_v = \Lambda - \Lambda_n$. As seen in Fig. 3b the exponential relaxation rate Λ_v (normalized at the lowest temperature to the Gaussian rate σ_v) yields essentially the same temperature dependence as does σ_v, with a linear increase below about 12 K.

The inset to Fig. 3a shows the temperature depen-

dence of $\lambda(T)$, extracted from Eq. 2. We see that the characteristic length scale for λ is $\sim$ 500 lattice constants ($a = b = 4.232$ Å [4]). Thus, if the muon makes $\sim$ 5 random hops in the 12μs duration of our experiment ($1/\tau \approx 0.4\mu\mathrm{s}^{-1}$) it moves only $\sim \sqrt{5}$ lattice spacings, and cannot affect the measurement of λ. We obtain an extrapolated zero-temperature penetration depth $\lambda(0) = 241$ nm. To obtain the Ginsburg-Landau penetration depth one must apply mean-free-path corrections: $\lambda_{GL} = \lambda(0)(1+\xi_0/l_{\mathrm{tr}})^{1/2}$, where l_{tr} is the transport mean free path [13]. We have estimated $l_{\mathrm{tr}} \approx 10$ nm using the values of the resistivity at $T = T_{\mathrm{c}}$, Sommerfeld constant, T_{c} and ξ_0 [4] and the formulas found in Ref. [14], so that $\lambda_{GL} \approx 265$ nm. We note that our direct measurement of $\lambda(0)$ is about $2\times$ that reported from critical field data [4], and that the magnitude of λ can depend on the fit function used [10]. Thus, our principal result is the linear *temperature dependence* of η_{s} (Eq. (2)), or alternatively, the low-temperature linaer behavior of $\lambda(T)$. As shown in Fig. 3a (inset) $\Delta\lambda(T) = \lambda(T) - \lambda(0) \propto T$ for $T/T_{\mathrm{c}} \leq 0.5$, within the statistical errors.

We now discuss the implications of our measurements for the symmetry of the superconducting order parameter in $PuCoGa_5$. The ZF μSR linewidth $\Delta(T)$ shows no change in magnitude below T_{c}. Thus, there is no evidence for a TRV superconducting order parameter, the signature for which is an increased linewidth below T_{c} arising from spin or orbital moments [15], as found in (U,Th)Be_{13} [16], Sr_2RuO_4 [17], and $PrOs_4Sb_{12}$ [18]. This means that the superconducting order parameter is a linear combination of basis functions for tetragonal symmetry with real coefficients.

In a superconductor whose electrons are paired in an $L = 0$ orbital angular momentum state the μSR rate σ_{v} or Λ_{v} is relatively temperature-independent below about $T/T_{\mathrm{c}} = 0.5$, reflecting exponentially-activated quasiparticle excitations over a superconducting gap which is nonzero over the entire Fermi surface [13]. This is clearly not observed in $PuCoGa_5$, as seen in Fig. 3b, where the two-fluid approximation [13] for s-wave superconductivity is plotted as the solid curve. Instead, the relaxation rate continues to increase linearly at low temperatures, yielding a low-temperature T-linear behavior for η_{s} and $\Delta\lambda(T << T_c)$. This behavior is quite generally associated with a line of nodes in the gap function for strong spin-orbit coupling (as expected for the heavy element Pu)[19] and local electrodynamics [20]; e.g., $\Delta\lambda(T) \propto T$ for $T^* < T \ll T_{\mathrm{c}}$, where T^* is a cross-over temperature $T^* \sim v_{\mathrm{F}}/\pi\lambda(0)$, below which T^3-dependence is calculated to occur due to non-local effects [21]. We estimate the Fermi velocity $v_{\mathrm{F}} \propto \xi_0 T_{\mathrm{c}} \approx 3 \times 10^6$ cm/s [14] and obtain $T^* \approx 1.8$ K. This is consistent with our results. A linear T-dependence has been found in a variety of copper-oxide high-temperature superconductors [10], and is associated with d-wave ($L = 2$) pairing (even parity, pseudo-spin singlet). In many heavy fermion superconductors d-wave pairing has also been established [22]. This particular gap symmetry is strongly enhanced by a spin-fluctuation pairing mechanism [6, 23], as opposed to electron-phonon pairing which favors s-wave pairing. Thus, our ZF and TF μSR studies in $PuCoGa_5$ show a gap symmetry which is similar to both the heavy fermion and copper-oxides superconductors [24], though $PuCoGa_5$ is neither particularly heavy nor is it an oxide. This behavior may be tied to the 2-dimensional character of its Fermi surface [7] which can enhance low-frequency spin fluctuations. Future μSR experiments are planned to investigate the field dependence of the superconducting symmetry of this material.

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